

Supplementary Information

The Mott-Schottky heterojunction MoC@NG@ZIS with enhanced kinetic response for promoting photocatalytic hydrogen production

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1. Experiment

1.1 Synthesis

All the chemicals were used without further purification. Triethanolamine (TEOA), $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$, ZnCl_2 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were purchased from Aladdin Reagent Co., Ltd. Thioacetamide (TAA), glycerol ($\text{C}_3\text{H}_8\text{O}_3$) and melamine ($\text{C}_3\text{H}_6\text{N}_6$) were supplied by Beijing J&K Scientific Co., Ltd.

1.1.1 Synthesis of MoC@NG

The samples of MoC@NG were synthesized by a simple solid-state reaction method. The 0.465 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 2.0 g $\text{C}_3\text{H}_6\text{N}_6$ were mechanically ground for 30 min. The obtained homogeneous mixture was calcined under N_2 atmosphere at 500 °C for 2 h with a heating rate of 5 °C min^{-1} , and finally sintered at 800 °C for 120 min. The preparation methods of $\text{Mo}_2\text{C@NG}$ and $\text{Mo}_2\text{C/MoC@NG}$ are similar to that of MoC@NG, except that the calcination times in the high-temperature section (800 °C) are 80 and 100 min, respectively.

1.1.2 Synthesis of NG

The 2.0 g $\text{C}_3\text{H}_6\text{N}_6$ and 0.878 g $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were mechanically ground for 30 min. The homogeneous mixture was first calcined at 500 °C for 2 h with a heating rate of 5 °C min^{-1} under N_2 atmosphere and then further sintered at 800 °C for 2 h.

1.1.3 Synthesis of ZnIn_2S_4

Typically, 0.055 g ZnCl_2 , 0.234 g $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and 0.24 g TAA were dissolved in 40 mL deionized water containing 20 vol% glycerol under vigorous stirring. After stirring for 30 min, the mixture was reacted in the water bath at 80 °C for 2 h. After cooling down to room temperature, the precipitates were collected by centrifugation and washed with deionized water and ethanol several times, and then dried at 60 °C overnight. The prepared samples were labeled as ZIS.

1.1.4 Synthesis of MoC@NG@ZIS hybrid photocatalyst

The preparation method of MoC@NG@ZIS samples is similar to that of ZIS. In detail, a certain amount of MoC@NG was ultrasonically dispersed into an aqueous solution (40 mL, 20 vol% glycerol) for 0.5 h. After that, 0.055 g ZnCl₂, 0.234 g InCl₃·4H₂O and 0.24 g TAA were dissolved in the solution and stirred for 1 h. Finally, the acquired solution was stirred and reacted in the water bath at 80 °C for 2 h. After natural cooling, the products were filtered and washed with deionized water and ethanol, and then dried at 60 °C overnight. The synthesized samples were marked as MoC@NG-x@ZIS (x = 5, 10, 15, 20, 25), and x represents the mass of MoC@NG (mg). The MoC@NG-15/ZIS represents the physical mixture of MoC@NG and ZIS. The Mo₂C@NG@ZIS, Mo₂C/MoC@NG@ZIS and NG-15@ZIS were synthesized under the same reaction conditions as MoC@NG@ZIS, but with Mo₂C@NG, Mo₂C/MoC and NG to replace MoC@NG, respectively.

1.2 Characterization

The crystal structure of photocatalysts was analyzed by X-ray diffraction (XRD, Rigaku Ultima IV, Japan) using Cu K α radiation (40 kV, 40 mA). The microscopic morphology was observed by field-emission scanning electron microscope (FE-SEM, SUPRA 55, Zeiss) and transmission electron microscope (TEM, JEM-2200FS, JEOL). Energy-dispersive X-ray spectroscopy (EDS) mapping was also obtained by TEM. The X-ray photoelectron spectra (XPS) were determined by an AXIS ULTRA DLD spectrometer using a monochromatic Al K α radiation ($h\nu = 1486.6$ eV). The texture properties of samples were characterized by Brunauer-Emmett-Teller (BET, ASAP 2460). The Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were measured with Shimadzu UV-2550. The steady-state photoluminescence (PL) spectra were implemented on the spectrophotometer (FLS1000) with an excitation wavelength of 340 nm. The time-resolved photoluminescence (TRPL) decay curves were measured by a fluorescence spectrophotometer (Edinburgh, FSL1000) using a 340 nm EPLED as an excitation light source.

A typical three-electrode cell using the CHI660E electrochemical workstation was employed to determine the photoelectrochemical performance. The photocatalysts (5 mg) were dispersed in an ethanol solution containing 10 vol% Nafion reagents. The mixed solution was uniformly deposited on a 1 cm × 1 cm FTO conductive glass as a working electrode, while the Pt sheets and Ag/AgCl electrodes were used as counter and reference electrodes, respectively, and 0.5 M Na₂SO₄ aqueous solution was used as the electrolyte. Electrochemical impedance spectroscopy (EIS) measurements were performed with the frequency from 0.01 to 100,000 Hz. The transient photocurrent was measured under the irradiation of 300W Xe lamp ($\lambda > 400$ nm).

1.3 Photocatalytic test

The photocatalytic hydrogen evolution experiments were carried out in a sealed quartz flask (50 mL). In a typical test, the photocatalysts (5 mg) were added into 20 mL 20 vol% TEOA aqueous solution with ultrasonic dispersion for 5 min. Before irradiation, the reactor was evacuated and filled with N₂ to ensure that it remained in an anaerobic condition. A 300 W Xenon lamp equipped with a UV cut-off filter ($\lambda > 400$ nm) was adopted as light source. The evolved H₂ was analyzed by a gas chromatograph (SHIMADZU GC-2014, TCD). The apparent quantum efficiency (AQE) was measured at monochromatic wavelengths (400 nm, 420 nm, 450 nm, 500 nm and 550 nm), and calculated according to the following equation:

$$\text{AQE} = \frac{N_e}{N_p} \times 100\% = \frac{2 \cdot N_{\text{H}_2} \cdot N_A \cdot h \cdot c}{W \cdot S \cdot t \cdot \lambda} \times 100\%$$

Where N_e represents the number of electrons participating in the reaction, N_p means the number of incident photons. N_{H_2} , N_A , h and c represent the number of evolved H₂ molecules, Avogadro constant, Planck constant and the speed of light. W , S , t and λ represent the irradiation intensity, the irradiation area, the reaction time and the wavelength of monochromatic light, respectively.

2. Figures

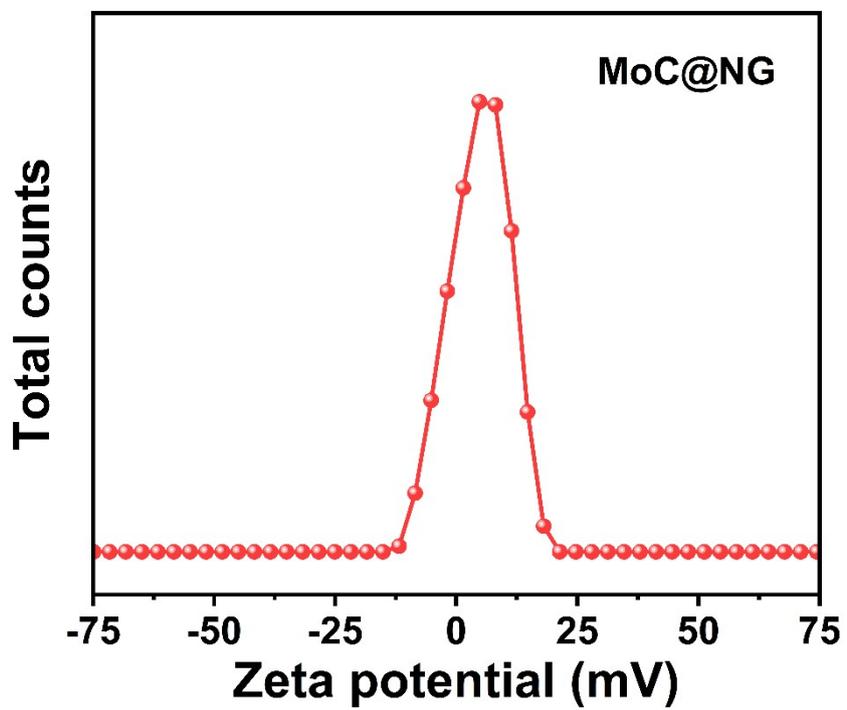


Fig. S1 Zeta potential of MoC@NG in deionized water at pH 7.

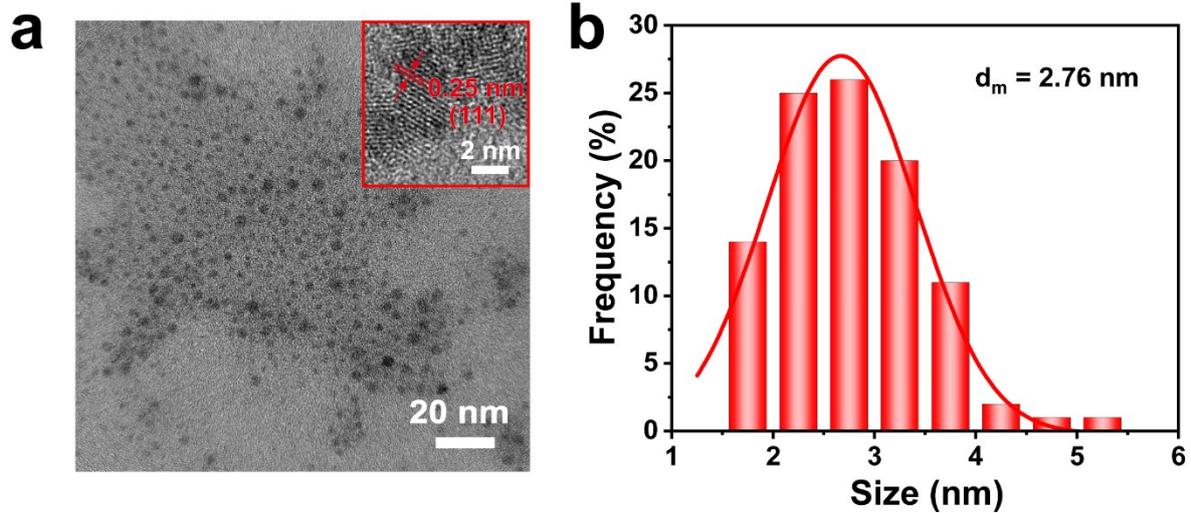


Fig. S2 (a) TEM image (the inset is the corresponding high-resolution TEM image) and (b) the particle size distribution of MoC@NG.

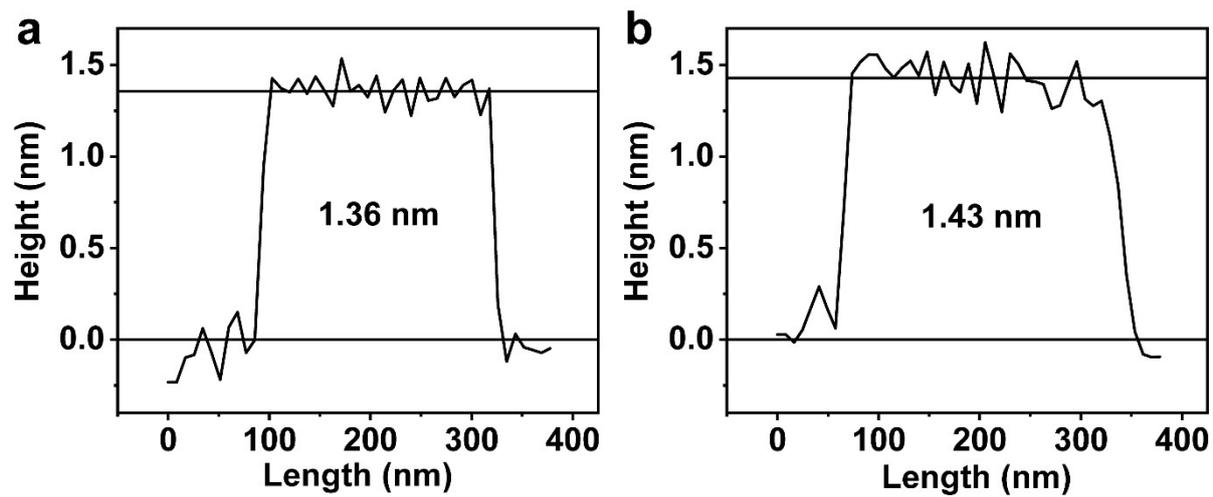


Fig. S3 The height patterns corresponding to AFM image of MoC@NG-15@ZIS.

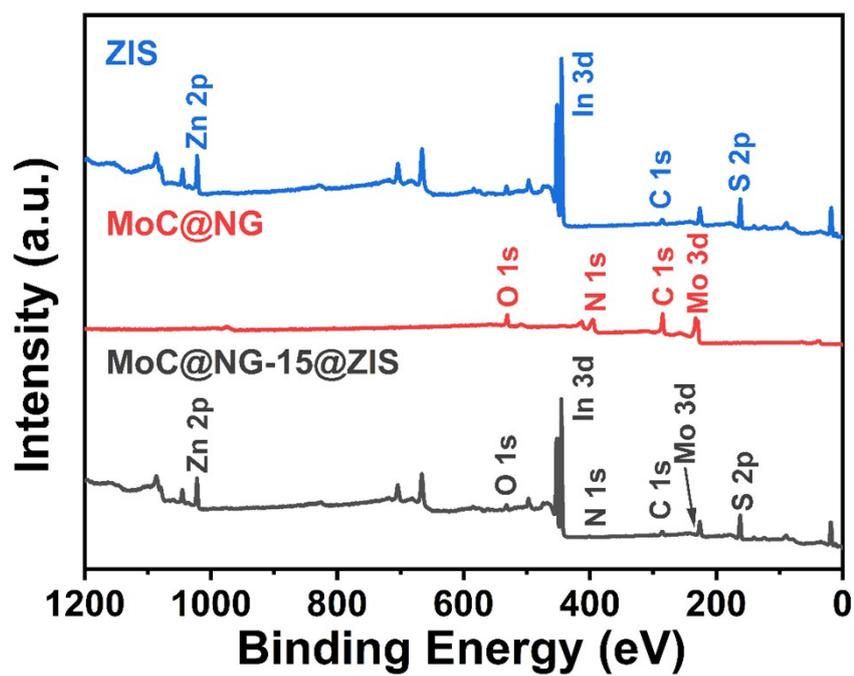


Fig. S4 The XPS spectra of MoC@NG, ZIS and MoC@NG-15@ZIS.

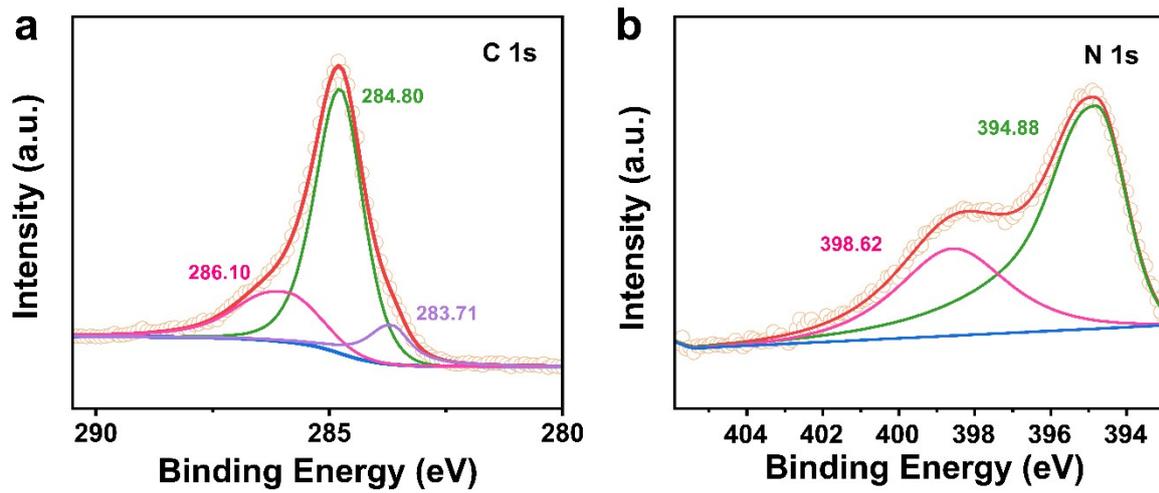


Fig. S5 The XPS spectra of C 1s and N 1s for MoC@NG.

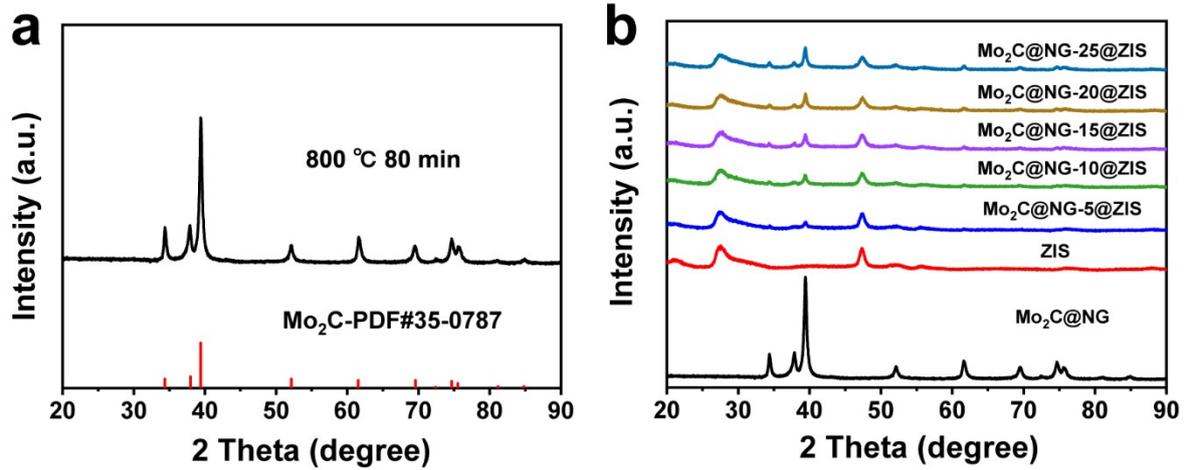


Fig. S6 The XRD patterns of (a) $\text{Mo}_2\text{C}@NG$ and (b) $\text{Mo}_2\text{C}@NG-x@ZIS$, $x = 0, 5, 10, 15, 20, 25$.

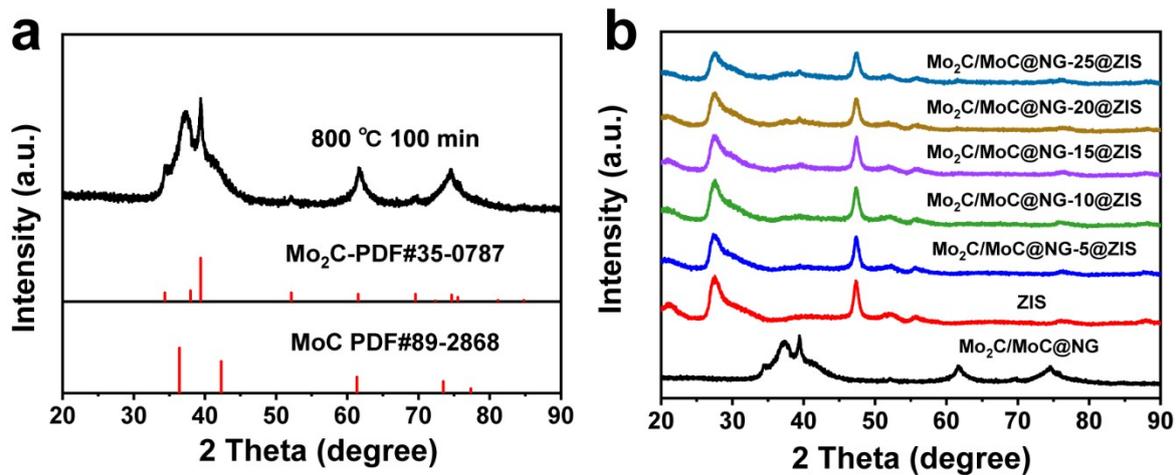


Fig. S7 The XRD patterns of (a) Mo₂C/MoC@NG and (b) Mo₂C/MoC@NG-x@ZIS, x = 0, 5, 10, 15, 20, 25.

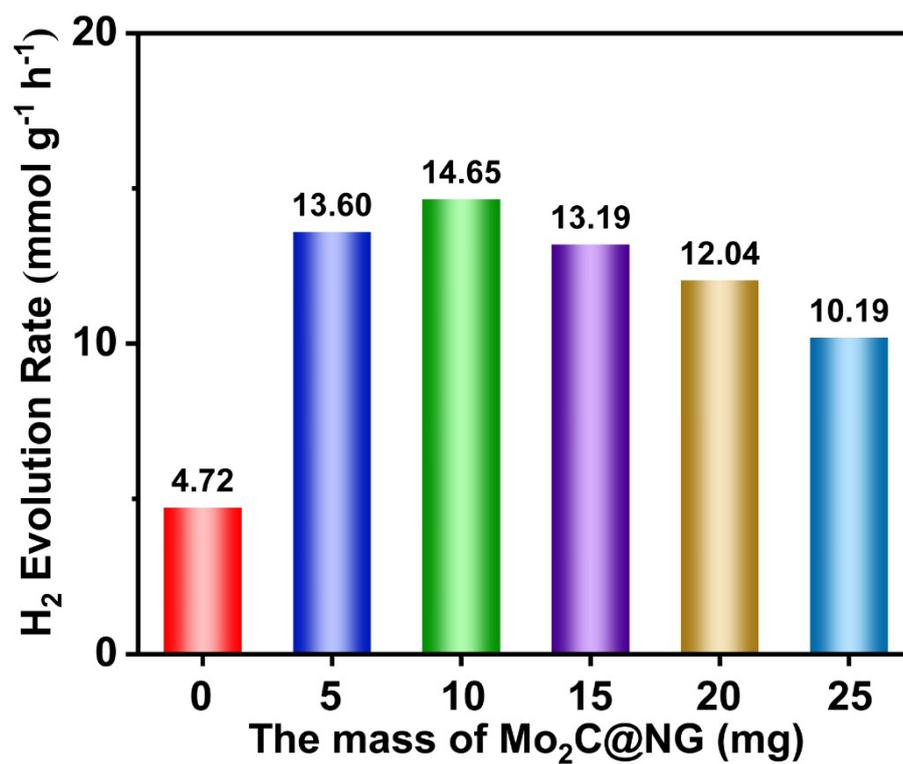


Fig. S8 Photocatalytic hydrogen production performance of Mo₂C@NG-x@ZIS, x = 0, 5, 10, 15, 20, 25.

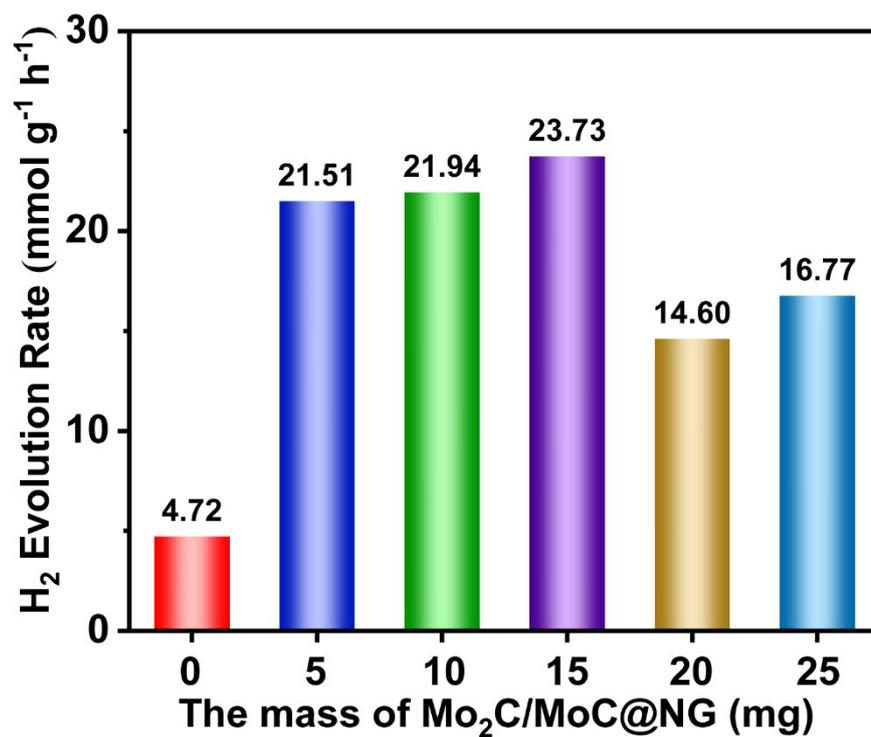


Fig. S9 Photocatalytic hydrogen production performance of Mo₂C/MoC@NG-x@ZIS, x = 0, 5, 10, 15, 20, 25.

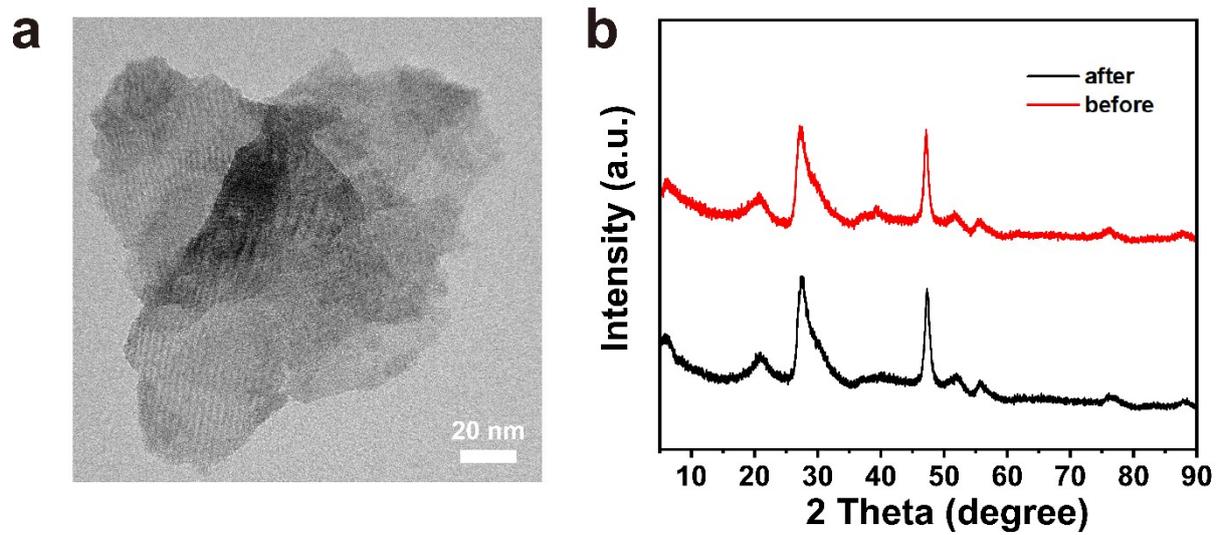


Fig. S10 (a) TEM image after cycles and (b) XRD patterns before and after cycles for MoC@NG-15@ZIS.

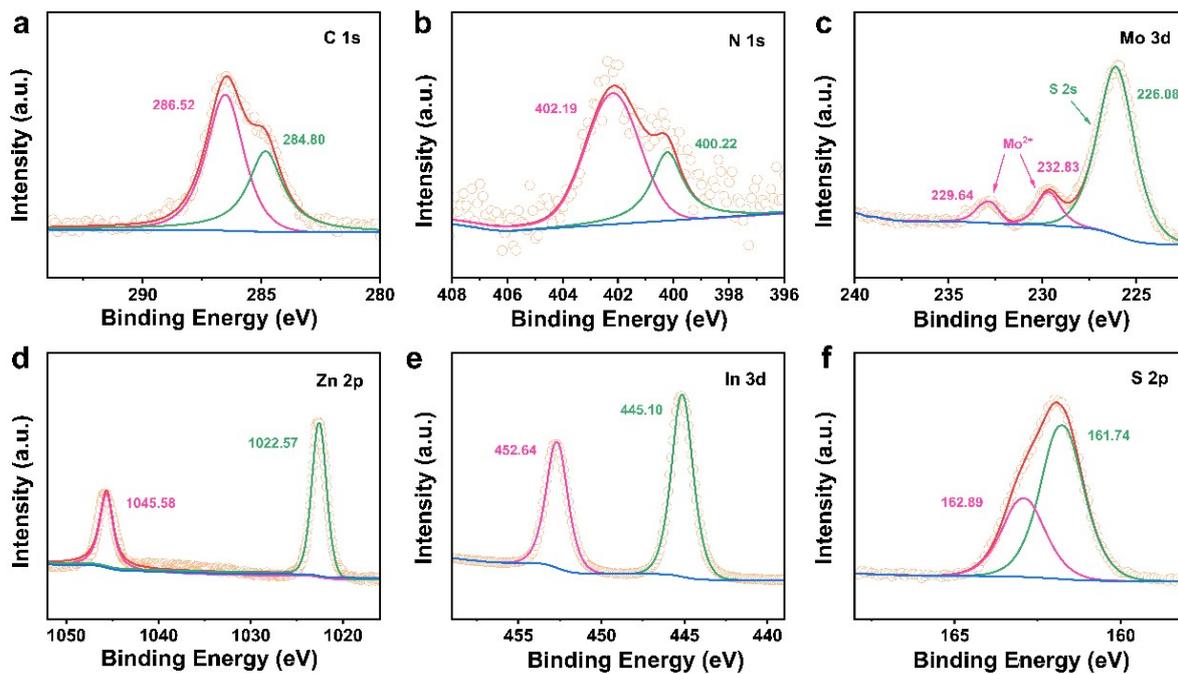
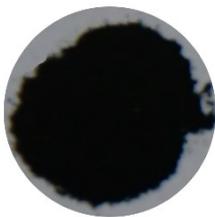


Fig. S11 XPS spectra of MoC@NG-15@ZIS after cyclic test. (a) C 1s; (b) N 1s; (c) Mo 3d; (d) Zn 2p; (e) In 3d; (f) S 2p.

MoC@NG



ZIS



MoC@NG-5@ZIS **MoC@NG-10@ZIS**



MoC@NG-15@ZIS **MoC@NG-20@ZIS** **MoC@NG-25@ZIS**

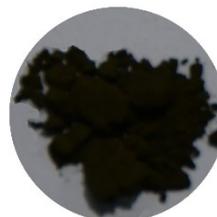


Fig. S12 Sample images of MoC@NG and MoC@NG-x@ZIS, x=0, 5, 10, 15, 20, 25.

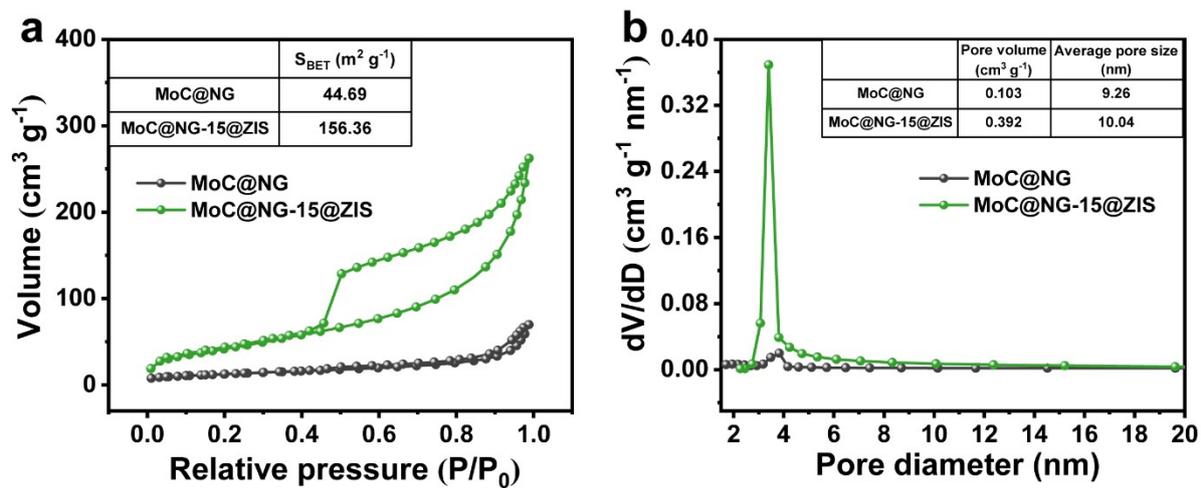


Fig. S13 (a) N_2 adsorption-desorption isotherms and (b) the pore size distribution of MoC@NG and MoC@NG-15@ZIS.

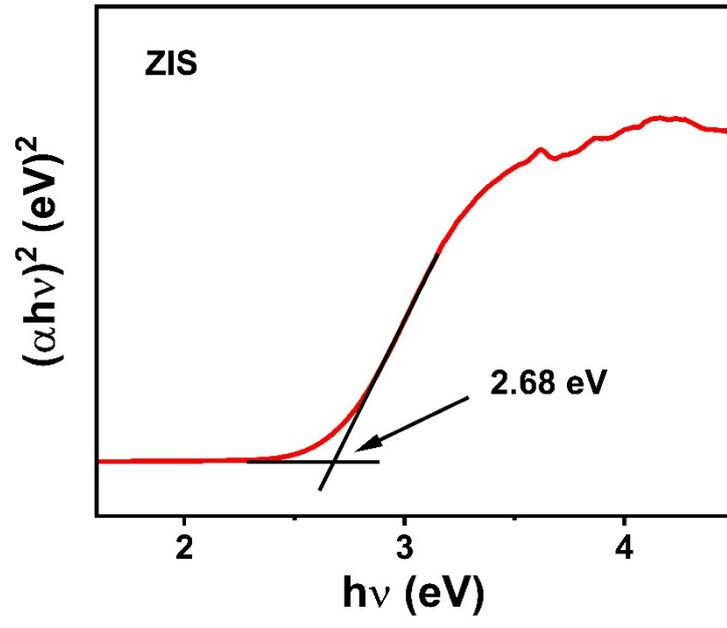


Fig. S14 Tauc plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) of ZIS.

3. Tables

Table S1 The AQE of MoC@NG-15@ZIS at different wavelengths.

Wavelength (nm)	400	420	450	500
AQY (%)	2.70	1.84	1.15	0.21

Table S2 List of the photocatalytic hydrogen production performance of photocatalysts in related systems.

Photocatalyst	Sacrificial agent	Cocatalyst/sensitizer	Activity (mmol g ⁻¹ h ⁻¹)	Light source	Ref
g-C₃N₄@ZnIn₂S₄	15 vol% TEOA	—	2.820	300 W Xe lamp (λ > 400 nm)	R ¹
Ti₃C₂T_x/ZnIn₂S₄	10 vol% TEOA	Pt	3.475	LED lamps (λ > 420 nm)	R ²
g-C₃N₄@ZnIn₂S₄	TEOA	Pt	4.854	300 W Xe lamp (λ > 400 nm)	R ³
Ni_{1-x}Co_xSe₂-C/ZnIn₂S₄	20 vol% TEOA	—	5.1	300 W Xe lamp (λ > 420 nm)	R ⁴
ZnIn₂S₄@PCN-224	Na ₂ S (0.35 M), Na ₂ SO ₃ (0.25 M)	—	5.68	300 W Xe lamp (λ > 420 nm)	R ⁵
ZnIn₂S₄@MoS₂	Na ₂ S (0.35 M), Na ₂ SO ₃ (0.25 M)	—	5.808	300 W Xe lamp (λ > 320 nm)	R ⁶
H_xMoO₃@ZnIn₂S₄	10 vol% TEOA	—	5.9	300 W Xe lamp (λ > 420 nm)	R ⁷
PBN/ZnIn₂S₄	20 vol%	—	5.946	300 W Xe	R ⁸

	TEOA			lamp (visible light)	
g-C₃N₄@ZnIn₂S₄-S	20 vol% TEOA	Pt	6.095	300 W Xe lamp (λ > 420 nm)	R ⁹
Ti₃C₂T_x/ZnIn₂S₄	20 vol% TEOA	—	7.420	300 W Xe lamp (λ > 400 nm)	R ¹⁰
g-C₃N₄@ZnIn₂S₄	20 vol% TEOA	—	8.601	300 W Xe lamp (λ > 400 nm)	R ¹¹
Co₉S₈/ZnIn₂S₄	10 vol% TEOA	—	9.039	300 W Xe lamp (λ > 400 nm)	R ¹²
WS₂@C@ZnIn₂S₄	20 vol% lactic acid	—	11.15	300 W Xe lamp (simulated sunlight)	R ¹³
Co/NGC@ZnIn₂S₄	20 vol% TEOA	—	11.270	300 W Xe lamp (λ > 400 nm)	R ¹⁴
g-C₃N₄@ZnIn₂S₄	0.1 M Na ₂ S/Na ₂ S O ₃	—	14.799	300 W Xe lamp (λ > 400 nm)	R ¹⁵
ZnIn₂S₄-MOFL	Na ₂ S (0.35 M), Na ₂ SO ₃	Pt	28.2	Simulated Sunlight Irradiation	R ¹⁶

(0.25 M)

Pt_{0.3}-ZnIn₂S₄	10 vol% TEOA	—	29.20	300 W Xe lamp (λ > 420 nm)	R ¹⁷
MoC@NG- 15@ZnIn₂S₄	20 vol% TEOA	—	32.96	300 W Xe lamp (λ > 400 nm)	This work

References

1. Z. Zhang, K. Liu, Z. Feng, Y. Bao and B. Dong, *Sci. Rep.*, 2016, **6**, 19221.
2. G. Zuo, Y. Wang, W. L. Teo, A. Xie, Y. Guo, Y. Dai, W. Zhou, D. Jana, Q. Xian, W. Dong and Y. Zhao, *Angew. Chem., Int. Ed.*, 2020, **59**, 11287-11292.
3. Z. Gao, K. Chen, L. Wang, B. Bai, H. Liu and Q. Wang, *Appl. Catal., B*, 2020, **268**, 118462.
4. Y. Chao, P. Zhou, J. Lai, W. Zhang, H. Yang, S. Lu, H. Chen, K. Yin, M. Li, L. Tao, C. Shang, M. Tong and S. Guo, *Adv. Funct. Mater.*, 2021, **31**, 2100923.
5. P. Jin, L. Wang, X. Ma, R. Lian, J. Huang, H. She, M. Zhang and Q. Wang, *Appl. Catal., B*, 2021, **284**, 119762.
6. Y. Peng, M. Geng, J. Yu, Y. Zhang, F. Tian, Y. n. Guo, D. Zhang, X. Yang, Z. Li, Z. Li and S. Zhang, *Appl. Catal., B*, 2021, **298**, 120570.
7. F. Xing, C. Cheng, J. Zhang, Q. Liu, C. Chen and C. Huang, *Appl. Catal., B*, 2021, **285**, 119818.
8. W. Zhang, S. Zhao, Y. Xing, H. Qin, Q. Zheng, P. Zhang, S. Zhang and X. Xu, *Chem. Eng. J.*, 2022, **442**, 136151.
9. Y. Qin, H. Li, J. Lu, Y. Feng, F. Meng, C. Ma, Y. Yan and M. Meng, *Appl. Catal., B*, 2020, **277**, 119254.
10. T. Su, C. Men, L. Chen, B. Chu, X. Luo, H. Ji, J. Chen and Z. Qin, *Adv. Sci.*, 2022, **9**, 2103715.
11. H. Yang, R. Cao, P. Sun, J. Yin, S. Zhang and X. Xu, *Appl. Catal., B*, 2019, **256**, 117862.
12. G. Zhang, D. Chen, N. Li, Q. Xu, H. Li, J. He and J. Lu, *Angew. Chem., Int. Ed.*, 2020, **59**, 8255-8261.
13. J. Huang, Q. Tian, H. Feng, C. Xue, J. Li and Q. Xu, *Chem. Eng. J.*, 2022, **447**, 137568.
14. S. Wang, Y. Wang, S. L. Zhang, S.-Q. Zang and X. W. Lou, *Adv. Mater.*, 2019, **31**, 1903404.

15. M. Tan, Y. Ma, C. Yu, Q. Luan, J. Li, C. Liu, W. Dong, Y. Su, L. Qiao, L. Gao, Q. Lu and Y. Bai, *Adv. Funct. Mater.*, 2022, **32**, 2111740.
16. Q. Zhang, H. Gu, X. Wang, L. Li, J. Zhang, H. Zhang, Y.-F. Li and W.-L. Dai, *Appl. Catal., B*, 2021, **298**, 120632.
17. X. Shi, C. Dai, X. Wang, J. Hu, J. Zhang, L. Zheng, L. Mao, H. Zheng and M. Zhu, *Nat. Commun.*, 2022, **13**, 1287.